GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

A26

Date: September 11, 1978

Project Title: ~~Study~~ the Mobility and Sorption Processes of Radioactive Waste Materials in Subsurface Migration

Project No: E-26-636 (Sub-project is B-522/Craft/ASL/EEAD)

Project Director: Dr. Geoffrey G. Eichholz

Sponsor: Pacific Northwest Laboratories, Battelle Memorial Institute

Agreement Period: From 3/1/78 Until 9/15/78

Type Agreement: Special Agreement No. B-56084-A-H (under DOE Prime Contract No. EY-76-C-06-1830)

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Reports Required: Monthly Progress Report; Organization Chart; Technical Progress Report; Workshop

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Defense Priority Rating: n/a

Assigned to: Nuclear Engineering (School/Laboratory)

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SPONSORED PROJECT TERMINATION

Date: 3/5/79

Project Title: Study the Mobility and Sorption Processes of Radioactive Waste Materials in Subsurface Migration

Project No: E-26-636

Project Director: Dr. G. G. Eichholz

Sponsor: Pacific Northwest Laboratories, Battelle Memorial Institute

Effective Termination Date: 9/15/78 (Fixed-Price)

Clearance of Accounting Charges: ---

Grant/Contract Closeout Actions Remaining:

- X Final Invoice and Closing Documents
- _ Final Fiscal Report
- X Final Report of Inventions
- X Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other _____

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SCHOOL OF NUCLEAR ENGINEERING

Atlanta, Georgia 30332 (404) 894-3720

GEORGIA INSTITUTE OF TECHNOLOGY

August 11, 1978

Dr. R. J. Serne
Manager
Waste-Geologic Media Interactions
Battelle Pacific Northwest Laboratories
P.O. Box 999
Richland, Washington 99352

Monthly Progress Report - Project E26-636
(Special Agreement B-56084-A-H)

Dear Dr. Serne:

After many months of delays we have received Special Agreement B-56084-A-H and it has been signed by Georgia Tech authorities. Although we have not received back the executed contract from BNWL, we are proceeding on the assumption that the project is properly funded as of August 1, 1978 and we are sending you this as the first report due.

Work has, in fact, been under way for some time in anticipation of your support funded by internal funds and consequently we expect to be able to meet contractual work requirements, at least in a preliminary fashion. We hope it will be possible to extend the contract into the next fiscal year without undue disruption to permit us to plan the work on a broader front.

The following activities can be reported to date:

Task 1: Procurement of Supplies

Orders have been placed for all the materials, supplies, and capital outlay items and much of the material is at hand.

Task 2: Set up Rock Columns and Detector System

Work to date has used sand rather than crushed rock.

A first column was fabricated all of plexiglass tubing, 1 1/2" inside diameter. The length of the sand bed was ~ 60 cm. The sand used was 20-80 mesh sifted and found on detailed analysis to be > 95% (mass) grains larger than 170 mesh. Attainable pore velocities under gravity feed were as high as 40 km/yr, so that control of the flow to useful velocities (~ 1 km/yr) would be difficult. Even at highest velocities, the flow through the pores was laminar, according to calculations.

√ c: Al Becker

The detection system used was one constructed for earlier experiments - a pair of G-M tubes mounted end-on facing the column with lead collimators of 1/2" slit width and 1/2" depth. Although their background was quite attractively low, collimation and detection efficiency were unsatisfactory.

A second type of detector, whose central feature is a 1/2 x 3/4" thick NaI(Tℓ), crystal has been obtained. Initial tests on it indicate that its sensitivity will allow much finer collimation with minimal count rate loss. Tests are continuing, but it is expected that detectors of this type will be used in future work.

A smaller plexiglass column with 1/2" inside diameter and a bed length ~ 15 cm has just been completed and filled with sand nominally 80-170 mesh. Its flow rate, though not accurately measured yet, will be much smaller than that in the initial column, and much easier to control to useful velocities. The smaller column will also allow the use of much smaller amounts of tracer and will simplify external scanner collimation. It is anticipated that future work will use columns of this size or slightly smaller.

Task 3: Fabricate Labelled Particles

Fine carrier particles have been made using a ball mill and grinding times of ~ 48-72 hrs. The materials ground to date are kaolinite, vermiculite, and silica, in various volumes. The most successful has been kaolin, for which several gallons of suspension with ~ 30 mg/ml fines have been prepared. Size measurement of these fines will occur soon, but virtually all are of sub-micron size.

It was found to be much easier to activate the intrinsic sodium content of the kaolin particles than to label them with Cs, as was the initial plan.

Since transit times through the larger column are less than an hour, the half-life of Na-24 is no drawback here and is actually helpful in managing the inventory of radioactive materials on hand and in increasing the frequency with which tests can be done on the column without changing the bed.

Vermiculite can be traced the same way, but experiments will be required to see whether the sand has a suitable internal tracer. External labeling with cesium and Pu tracer, to simulate waste absorption, will be resumed once column behavior is well established.

Task 4: Execute Column Leaching Tests

Activated kaolin particles have been injected into the larger column, followed through it using the scanning detectors, and measured in the effluent using a NaI(Tℓ)-based system. No obvious retardation of the particles was observed, perhaps due to the relative sizes of the particles and the bed pores.

A cationic tracer has been used in separate tests and has also been followed through the bed and detected in the effluent. Simultaneous test with an anion, a cation, and particulates are planned for the near future.

Task 5: Initial Pu-Particle Rock Column Tests

Use of the Pu-237 tracer to date has been confined to determining its photon spectrum with greater accuracy than it is presented in the standard references and to using it for the testing and intercomparison of competing scanning detector systems.

Tasks 6 & 7: Preparation of Progress Report and Seattle Presentation

Photographs have been taken of some of the equipment for report illustrations and slides.

We believe we are making some progress. Please let me know if you require additional information.

Yours truly,

Geoffrey G. Eichholz
Regents' Professor

jhr

cc B. G. Wahlig
T. F. Craft
N. McHan

E-26-1036

September 19, 1978

Dr. R. J. Serne
Manager, Waste-Geologic Media Interactions
Battelle Pacific Northwest Labs.
P.O. Box 999
Richland, Washington 99352

Special Agreement No. B-56084-A-H

Dear Dr. Serne:

In accordance with the above agreement we are sending you herewith two copies of the draft report as required for your approval. I trust you will find it satisfactory as to content and format.

Please call me or Mr. Wahlig if there are any questions, at (404) 894-3722.

Yours truly,

G. G. Eichholz
Regents' Professor

GGE:rs

cc F. P. Fabro
N. McHan
T. F. Craft

KC: A+B, w/Rpt

JKR

MOBILITY AND SORPTION PROCESSES OF RADIOACTIVE WASTE MATERIALS IN SUBSURFACE MIGRATION

Draft Final Report
Spec. Agreement B-56084-A-H
Prime Contract EY-76-C-06-1830

by G. G. Eichholz and B. G. Wahlig

to Pacific Northwest Laboratories
Battelle Memorial Institute

School of Nuclear Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

September, 1978

Introduction

The safe disposal of high-level radioactive wastes is much in the public eye these days and in response to this interest, several major programs have been launched to identify suitable disposal sites, to qualify waste treatment processes as to effectiveness, permanence and cost, and to study possible migration paths and movement mechanisms by which a small portion of any buried solidified waste might conceivably be returned to the surface over a fairly long period of time. It is this latter problem area which is the subject of the DOE Prime Contract of which the present project constitutes a segment.

At the present time one envisages the disposal of solidified high-level radioactive wastes, preferably in processed and concentrated form, in deep crustal locations in artificial cavities in bedded salt or bed rock. Following a postulated incursion of water one may assume a slow leaching effect on the solid wastes, particularly if any crack development has occurred due to thermal or rock mechanical stresses, devitrification or anisotropic expansion effects. The slow movement of trace concentrations of waste products may then proceed in the form of tiny granules of solid waste or in soluble form. In the latter case dissolved ions would be expected to adsorb or plate out on exposed rock surfaces, shale or clay layers or on other fine particulates that may be present, suspended, in the aquifer. In the latter case, previous work at Georgia Tech has shown that radioactive pollutants may travel considerable distance, not necessarily at the velocity of the water, through a permeable bed layer. The present work has been directed to the study of two related phenomena:

1. the movement of submicron particles of a type expected near disposal

sites through aquifers of appropriate characteristics, and, 2. the sorption processes associated with the uptake of waste ions in trace concentrations on submicron particles and the measurement of subsequent partition coefficients leading to competitive transfer from the particles to surrounding bed media.

Owing to extended delays in contract negotiations, the work under the the project did not get formally under way until August 1, 1978. Related work, however, has been underway on a lesser scale for some time under Georgia Tech auspices, so that the present report summarizes various measurements done in this context both before and since the initiation date. Because of the limited scale of the work, most data reported here must be considered to be preliminary in nature only.

Project Objectives

The purpose of the continuing project is the determination of all parameters that affect the long-range movement of trace concentration waste products from subsurface depositories by way of suspended particles. The particles are assumed to be naturally present in the aquifer from eroded rock material or colloidal aggregates, and to provide sorption sites for dissolved waste ions. The aqueous medium is de-aerated "pure" water, possibly modified by prolonged contact with fractured surrounding rock faces, or slightly saline water in the case of bedded-salt repositories.

Factors that would be expected to affect mobility of the particulates are:

- particle size and surface area
- bed medium permeability
- bed pore size
- flow rate of water
- temperature
- particle material
- bed material
- particle shape
- dielectric properties of particles.

Factors that would be expected to affect adsorption and desorption of trace material would include:

- particle surface area
- particle ion exchange capacity
- trace element concentration
- impurity concentration in water (hardness)
- pH and E_h

valence of trace ions

K_D of bed medium

temperature

desorption parameters (concentration, displacement)

possible recoil effects

The work naturally falls into two major categories with various subtasks:

1. Mobility of particulates in permeable media

   pure water, saline water

   major trace elements (Pu, Tc, Zr, Cs)

   various particulates (clays, rock particles)

   various bed media (sand, rock, shale)

2. Sorption of trace elements on and off particulates

   various particulates and sizes

   pH, E_h of solution

   trace elements (as above)

   concentrations

   sorption rates

   surface area determinations

So far most of the work has concentrated on the first category, including the setting up of flow columns, the study of particulate movement, and the determination of detector sensitivity and resolution. However, work has been done on particle preparation and sizing, and some preliminary uptake studies. This work will be described in detail in the following sections.

Procedures and Methods

The tests on fine particle migration were made in columns containing beds of sand (for flow testing) or crushed rock (for sorption experiments)

through which particle-bearing solutions are allowed to flow. While the artificial fissure method of modeling field conditions has proved successful in studying dissolved radionuclides,[1] the affinity of fine particles for the surfaces under study is expected to be much smaller. Thus, columns of crushed rock are thought to be the most convenient way to provide sufficient numbers and path length to have a measurable effect upon particle behavior. The design and construction of the columns themselves will be discussed more fully below.

Water flows through the columns under the influence of gravity at pore velocities on the order of 10 km/yr. (In future experiments, metering pumps now on order will be used to drive the flow, which will allow better control of the flow at these or lower flow rates.) Traced particles in 1-2 m of water are injected by hypodermic syringe through a septum at the column inlet. The progress of the particles through the column is monitored in two ways--by external scanning detectors described below, and by counting successive portions of the column effluent.

The effluent counts are standardized to make it possible to calculate the fractional recovery of the injected tracer. For the two sizes of columns to be described below, the procedures for standardization differ as explained below. In both cases, the syringe is weighed before and after taking up the suspension of traced particles, after a portion is reserved for a standard, and after injection of the remainder of the tracer into the column. Knowing the masses of the standard and injected tracers and counting the standard in the same way as the effluent portions, one can relate the net count rates of the effluent to the total activity injected.

For the large column, the effluent portions are 20-50 mℓ, collected in disposable graduated beakers. The actual volume according to the graduations is recorded (for calculating concentrations) and the sample is brought to 50 mℓ total volume. All samples, including the calibration standard, are counted in 50 mℓ volumes. For the small column, it is more convenient to collect the samples in planchets, in fluid volumes of 1.2-3.5 mℓ. The samples are weighed immediately after collection and are then dried and reweighed to compute the sample volume. (The specific gravity of the samples is assumed to be a constant 1.0, although it must actually vary slightly from sample to sample. The total mass of the injected particles is only about 50 mg, however, and when distilled water is used to elute 50 or more samples, the error of assuming constant unit density is negligible.) All samples, including the calibration standard, are then counted as dried cakes in the planchets.

To date, only the natural sodium content of the particles has been used to trace them. This is convenient in testing equipment performance since activation to Na-24 in the Georgia Tech Research Reactor provides a readily available, inexpensive tracer of short half life. After about one week, unsatisfactory equipment can then be disassembled and modified without the need for decontamination. This tracer also suggests itself because high specific activity can be obtained, which is important in the detection of small portions of a 50 mg sample. Finally, the ready detectability of its gamma rays is an asset.

It is recognized, however, that this method will not be satisfactory for the main experimental activity, because the quality of interest is the behavior of radionuclides initially adsorbed on the surfaces of particles, and not the behavior of the particles themselves. On the bulk of the

experiments, then, Pu-237, Np-235, and perhaps Tc-95, obtained in the regular contractor distribution, will be the tracers of interest.

It may also prove desirable to follow both the particle and the adsorbed radionuclides in future experiments. While this may present certain logistical problems in obtaining the use of the requisite multichannel analyzers, it may also be the best alternative to the routine filtration of many small samples for which the initial volume of the sample as well as the activities of both the filter and the filtrate would have to be determined. The choice between these two possibilities has not yet been made.

Description of Apparatus

Columns

Two prototype columns have been constructed to date. Scale drawings of them are given in Fig. 1. Both are constructed of acrylic plastic tubing and sheet to minimize chemical interactions between the columns and the circulating solutions and to make visual inspection of the beds inside convenient. In constructing the prototypes it was necessary to use some brass fittings because of their ready availability, but polyethylene fittings are on order for use in the experimental columns. The only non-plastic materials expected to contact the solution in the experimental columns will be the rubber O-ring gaskets between the column flanges and their respective end caps, the fiberglass screen cemented over the entry hole in each end cap, and the iron-filled epoxy cement used throughout as cement and scalant. Each end cap is bolted to its respective flange in six places.

A large column, with 1 1/2" inside diameter (ID) and 27" bed length

was built first. According to published results on flow of fluids through beds of spheres packed in containers,[2] local velocity effects become negligible when the container to grain-diameter ratio (O/d) reaches 30-40. Thus there is a considerable margin of safety in using sand with a geometric mean size of 244 μm (0.0096 in., or $D/\bar{d}$ = 156) for the bed in this column. The bed itself consists of 24 in. of this sand, restrained on each end by approximately 0.6 in. of 16-20 mesh crushed granite, 0.8 in. of 10-16 mesh granite, and the screen cemented to the end cap. Typical parameters for these beds are 37% porosity, 0.03 cm/sec permeability (both measured), and a calculated average effective pore size of approximately 50 m.

Since it is desirable that the effluent from the column be representative of the flow through the whole cross-section of the bed, the end caps used initially incorporated mixing chambers of approximately 55 m each. Some refluxing occurred in these chambers, however, as was readily visible with a $KMnO_4$ visible tracer. This effect is quantified in Fig. 2, which compares the elution profile of an injection of activated kaolin particles for the large column with the mixing end caps initially used and the non-mixing end caps shown in Fig. 1. It is clear that although the total fraction of tracer carried through in the two cases is similar, the mixing end volumes smeared the elution profile over a larger volume even though the interactions between the particles and the bed grains were unchanged. For this reason, the mixing end caps were eliminated.

The injected particles were not especially strongly affected by the bed, however, and behaved quite similarly in their elution profiles to an injection of an ionic tracer $^{24}Na_2CO_3$, as shown in Fig. 3. Although a smaller fraction of the kaolin than of the Na_2CO_3 was recovered, the

particles were not significantly delayed compared to the ionic front.

Thus, it seemed desirable to use smaller grains in the bed to decrease the average pore size. Particles would then spend more of their time near grain surfaces, with correspondingly greater probability of attraction. The finer grains allowed the use of a smaller column also illustrated in Fig. 1. When this 0.5 in. ID column is loaded with 170-80 mesh (i.e., 88-178 m diameter) grains, the minimum D/d ratio is 71, well within the range of acceptable local velocity effects. In this column, 17.5 in. of fine sand is restrained on either end by 0.5 in. of coarse sand, 0.5 in. of 16-20 mesh granite, 0.5 in. of 10-16 mesh granite, and the fiberglass screen over the end cap opening. Typical parameters for such a bed are 40% porosity, 0.008 cm/sec permeability and average effective pore diameter of 23 m.

The increased ability of the small column to restrain fine particles is shown in Fig. 4., which compares the elution profiles for kaolin in the large and small columns, normalized to eliminate the effect of their volume difference. Although similar total fractions of the tracer are recovered in the two cases, the small column clearly makes the retardation of fine particle migration a visible effect. However, the behavior of cations (as observed in a $^{24}Na_2CO_3$ test) is not much different from that of particulates, as was observed in the large column. This is shown as Fig. 5. Besides having a greater effect on migrating species, the small column size also economizes on the use of bed material and radiotracer, and provides for less attenuation of radiation within the bed when an external scan is being taken. It is therefore anticipated that all future columns will be standaradized versions of this smaller column, containing relatively fine grains of the medium of interest.

Detectors

Two kinds of scanning detectors have been tested. The first type is a Victoreen Thyrode thin-walled G-M tube in an end-on shield. This type was intended for use with the small column and is shown in several different views in Fig. 6. The shield provides 1.59 cm of lead around the whole length of the tube. Collimation is provided by a 1/2 in. x 1/2 in. square groove across the face of the shield. Fig. 6. also shows the rack provided for reproducible positioning of the shielded detectors when scanning the column. The overall effect is a rugged, inexpensive detector, whose chief problems are poor collimation and only moderate detection efficiency. Unfortunately, improving the collimation rapidly degrades the detection efficiency. Of course, the G-M detector is also incapable of energy discrimination.

Therefore, a change has been made to the Harshaw M12SHA3/3/4-X, a self-contained 0.472 in. x 0.500 in. thick NaI(Tℓ) collimated scintillation crystal assembly* (originally designed for brain scanning). It was found experimentally that even with stricter collimation (3/8 in. wide x 1 in. deep compared to the 1/2 in. x 1/2 in.), the NaI detector was more sensitive than the G-M detector at photon energies up to 1.25 MeV, and is more sensitive by a factor of 5 for the low-energy photons from Pu-237. Although this system is considerably more expensive than the G-M system, its improved sensitivity, ease of collimation, and capability of energy discrimination make it preferable for the external scanning of the column. Therefore, the NaI detectors will be used for scanning in future work. Preliminary measurements have been done but improved collimator and positioning apparatus designs for the scanner are not yet completed.

The effluent detector is a 2 in. x 2in. NaI(Tℓ) detector housed in a stack of 2 1/1 in. radial width Pb shield rings. Its output is currently being counted simply in the discriminator mode, although pulse-height analysis may be employed in the future.

Fine Particles

One of the most important parts of this project is the preparation and characterization of suspensions of fine particles which will serve as carriers for radiotracers in the column experiments. To date, stable suspensions have resulted from the prolonged ball milling of kaolin, vermiculite, and silica. Samples of the suspensions obtained thusfar are shown in Fig. 7. In each case, the goal has been to create particles whose diameters are less than 1-2 μm.

Thusfar, the most success has been gained with kaolin. Approximately 100 mℓ of fine kaolin was ball milled in a one-quart ceramic jar about two-thirds filled with grinding balls and brim-full of distilled water. After 48 hrs. of milling, the fluid contents of the jar were poured off, the jar was rinsed out, and the resulting liquid was diluted to approximately 3 liters. This was allowed to settle for ~2 days and was then poured into a glass carboy. Approximately 25ℓ of suspension have been generated in this way and have remained opaque far about two months. The kaolin content of the suspension is ~ 30 mg/mℓ.

Raw (i.e., not heat-treated) vermiculite has been treated in a similar way, but has proven more resistant to grinding than kaolin. About 25ℓ of slightly cloudy suspension have been generated, but the vast majority of the solids generated are slightly too heavy to suspend stably--they settle out in times from two days to two weeks. Recycling these solids for

further milling has yielded some success.

In view of the difficulties encountered in grinding the two clays there is some doubt about the identity of the particles in the suspension resulting from grinding silica sand. Silica is much the hardest of the three minerals (Mohs' hardnesses are: kaolin, 2-2.5; vermiculite, 1/5; quartz. ~7).[3] The suspicion is, then, that the particles in the suspension may be the results of abrasion of the grinding jar, and not silica at all. This possibility is further reinforced by the grinding of Culebra dolomite (hardness 3.5-4.0) under the same condition led to no stable suspension of particles. Thus, x-ray diffraction analysis of all the suspensions would appear to be in order to verify the identities of the particles; this has not yet been arranged for.

In order to further specify the experimental conditions, the suspensions will also be analyzed using a computerized laser light-scattering system, which will measure the number average particle diameter. This system currently has a backlog of work which has prevented its use in this project so far.

The particles may also be analyzed using a high-voltage electrophoresis unit constructed for this purpose and shown in Fig. 8. with its power supply. It remains to be seen whether the pore sizes of available chromatography papers are sufficiently large to permit particle migration and whether a satisfactory method for particle detection can be arrived at.

The next experiments to be undertaken will involve attempts to tag the particles with Pu-237. These await the arrival of water purification and testing equipment currently on order. It is vital to reproducibility that the water used in making the solutions start out pure and that

that the water used in making the solutions start out pure and that conditions such as pH and total ionic strength be under control, since it may be expected that these will strongly affect the mechanisms and the reversibility of the sorption processes.

Pu-237 Spectrum

A final word is in order on the x-ray emission spectrum of Pu-237. Since many of the standard references carry very sketchy descriptions of the photon spectrum, it was important to measure the energies and relative intensities with some accuracy to facilitate the choice of useful detection systems. The spectrum resulting from this determination is shown in Fig. 9. The region of interest in this spectrum was calibrated using five peaks from Ga-133 (53.17 and 80.88 keV), Cd-109 (88.04 keV), and Co-57 (122.08 and 136.49 keV), none of whose measured energies differed by as much as 0.2 keV from their accepted values in separate measurements before and after the Pu-237 spectrum was accumulated. This is notable chiefly because personal communication with Dr. John Hines of Argonne National Laboratory has revealed that ANL's measured energies for Pu-237 photons are all almost precisely 5.0 keV higher than those shown in Fig. 9. This difference, while not material to any of the goals of this research, remains unresolved.

Conclusions

Because of the late date of finalization of the research contract and, hence, the limited manpower devoted to this project until recently, the results obtained so far are largely preliminary in nature. Work done has included some of the following:

setting up of two types of columns with detector systems;
determination of sensitivity and spatial resolution of the collimated GM and scintillation detectors
preparation of suspensions of kaolin particles
measurement of particulate movements through the bed with neutron-activated particles
determination of the Pu-237 γ-ray spectrum
planning of the next phases of the work, using several columns and a larger research group.

It is felt that reasonable progress has been made in getting ready for the major measurement program. Additional project personnel has been lined up and further equipment and supplies are being procured.

The results obtained so far illustrate the kind of differential movement between soluble tracers and active particulates that takes place in a permeable rock medium. It is hoped to obtain more definite results on the parameters concerned in the near future.

References

1. S. Fried, A. Friedman, J. Hines, R. Atches, L. Quarterman, and A. Volesky, "The Migration of Plutonium and Americium in the Lithosphere," Actinides in the Environment, A. C. S. Symposium Series no. 35, 19-46 (1976).

2. W. A. Gray, The Packing of Fine Particles, Chapman and Hall Ltd., London, 1968.

3. R. Kretz, "Physical Constants of Minerals," CRC Handbook of Chemistry and Physics, 58th Edition, CRC Press, Inc., B-214-B-219, 1977.

Figure Captions

Fig. 1 Diagram of Prototype Columns

Fig. 2 Electron of Particulate Tracers in the Large Columns with "Mixing" and "Non-mixing" End Caps

Fig. 3 Electron of Ionic and Particulate Tracers in the Large Column

Fig. 4 Electron of Particulate Tracers in the Large and Small Columns

Fig. 5 Electron of Ionic and Particulate Tracers in the Small Column

Fig. 6 Views of the Large Column and the Collimated Detector

Fig. 7 View of Mineral Suspensions

Fig. 8 High-voltage Electrophoresis Unit and Associated Power Supply

Fig. 9 Plutonium-237 Gamma-ray Spectrum Ge(Li) Detector and 1096-channel MCA

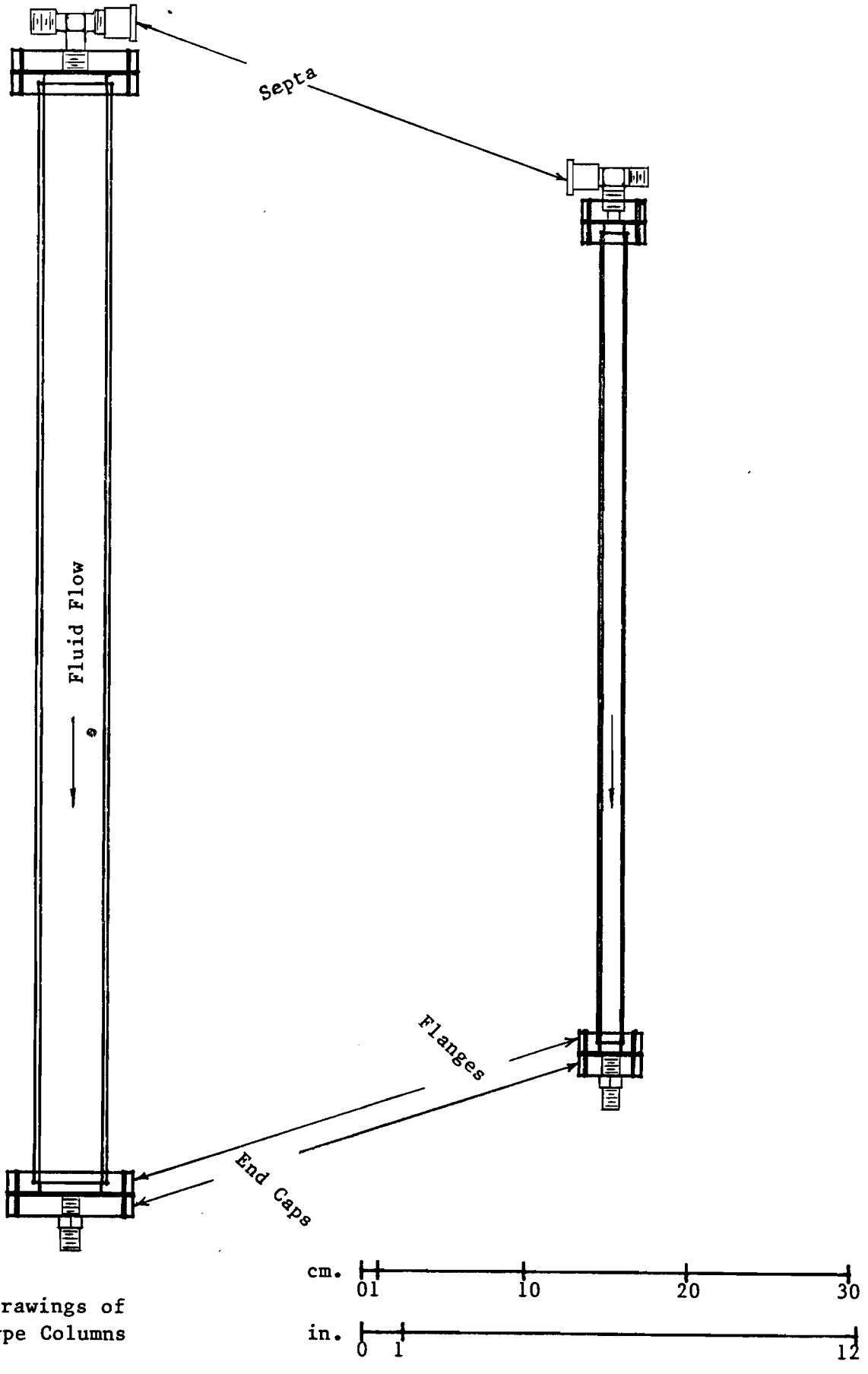

Fig. 1. Scale Drawings of Prototype Columns

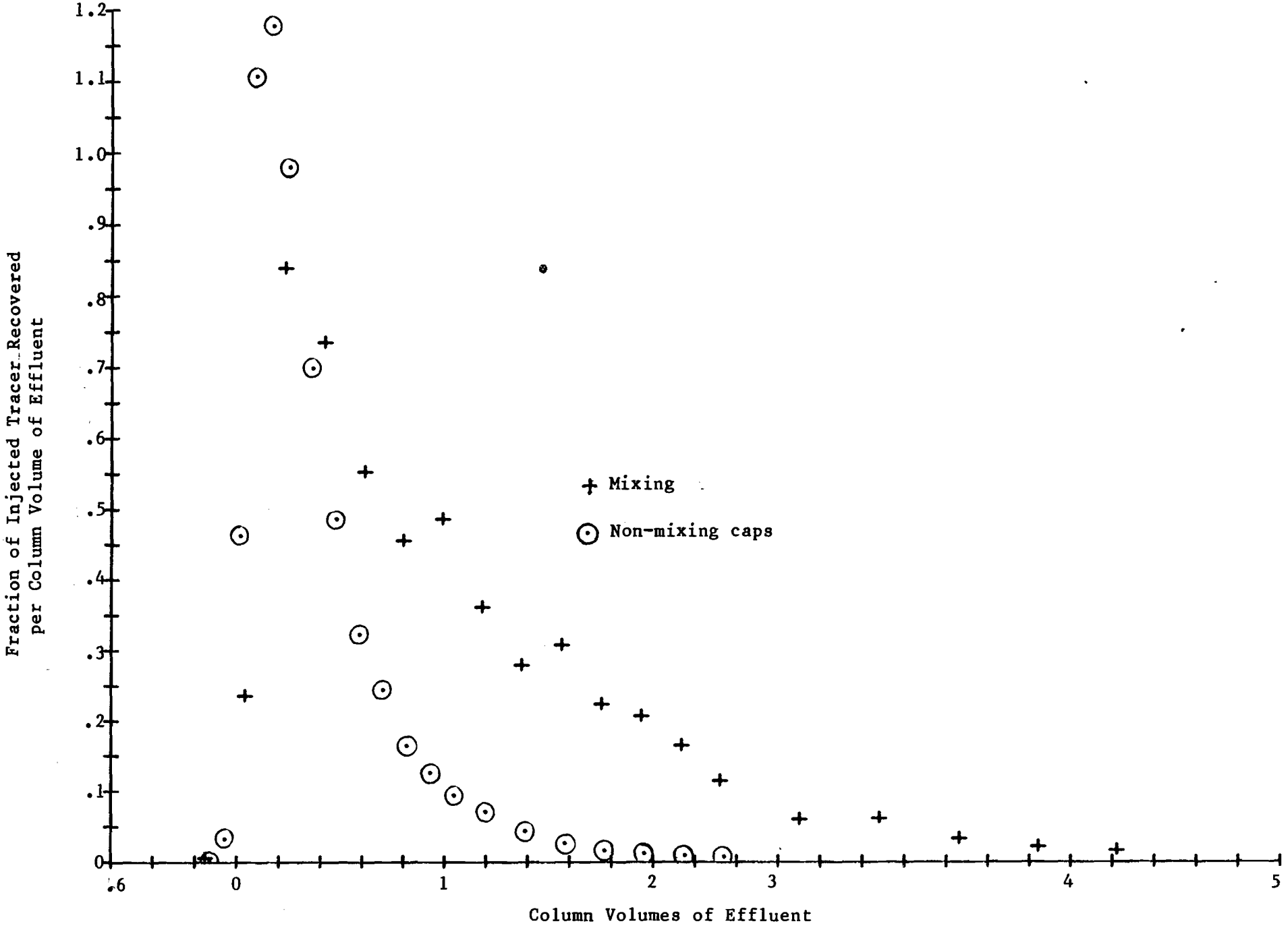

Fig. 2. Elution of Particulate Tracers in the Large Column with Mixing and Non-Mixing End Cap

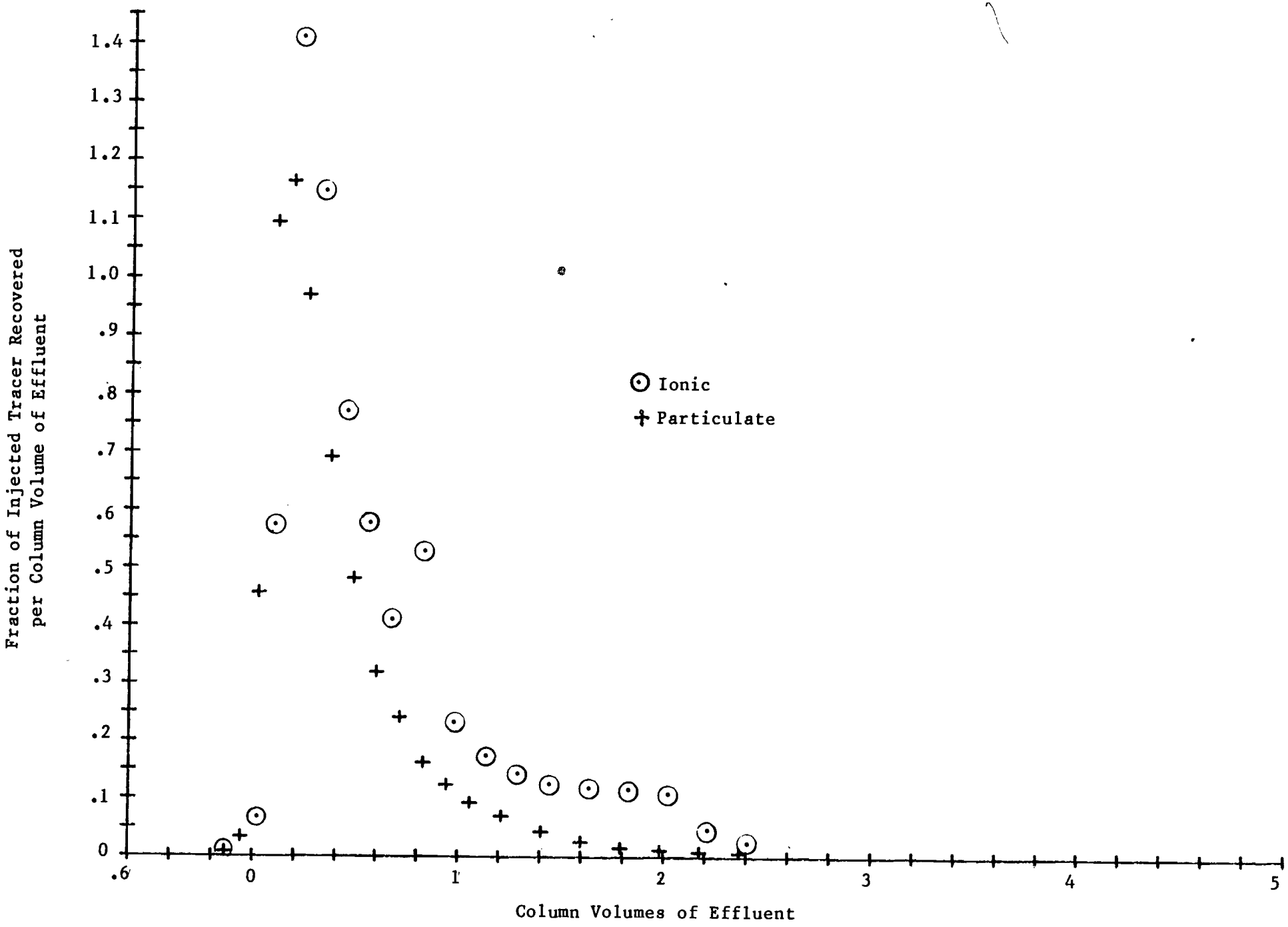

Fig. 3. Elution of Ionic and Particulate Tracers in the Large Column

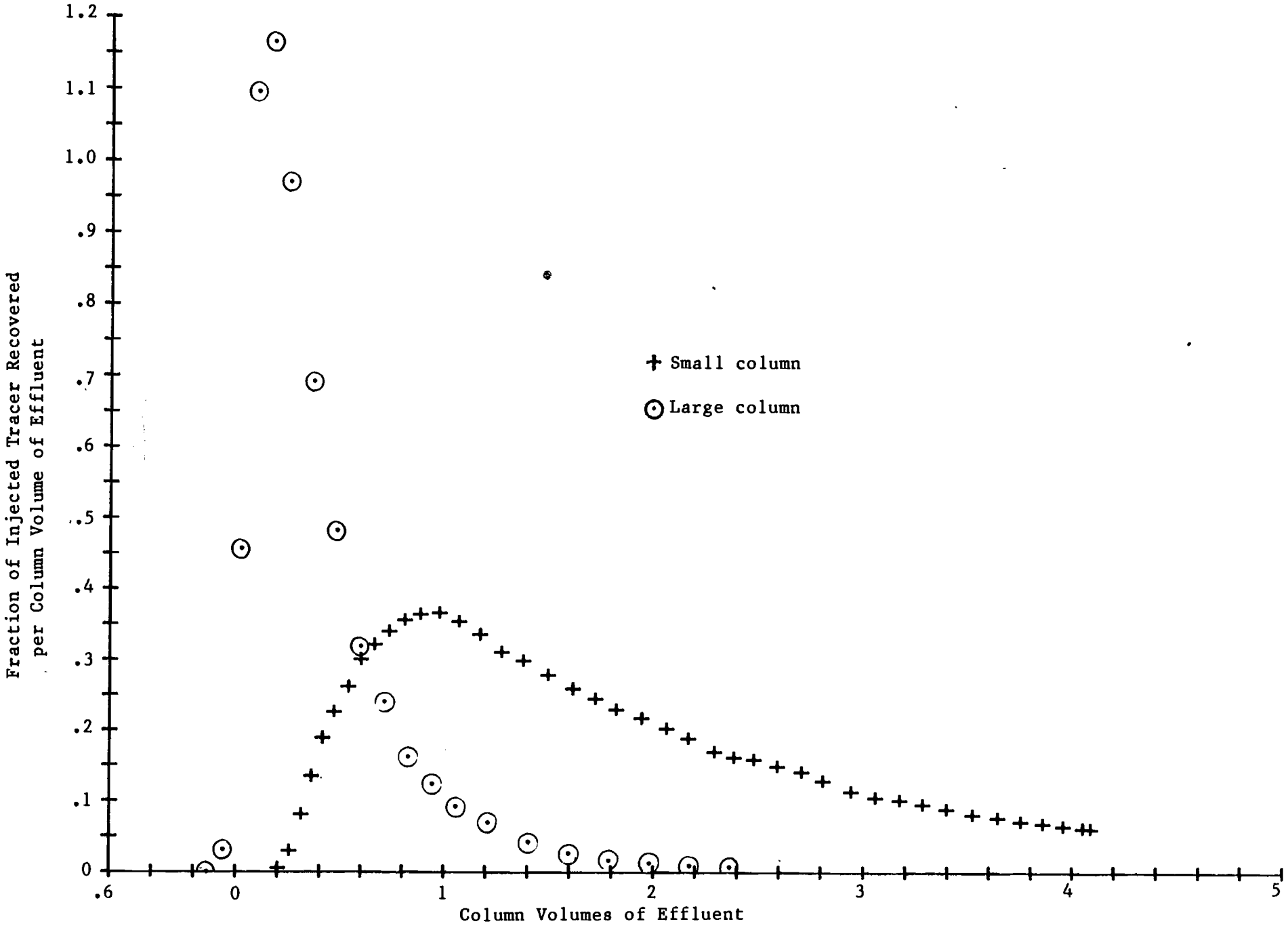

Fig. 4. Elution of Particulate Tracers in the Large and Small Columns

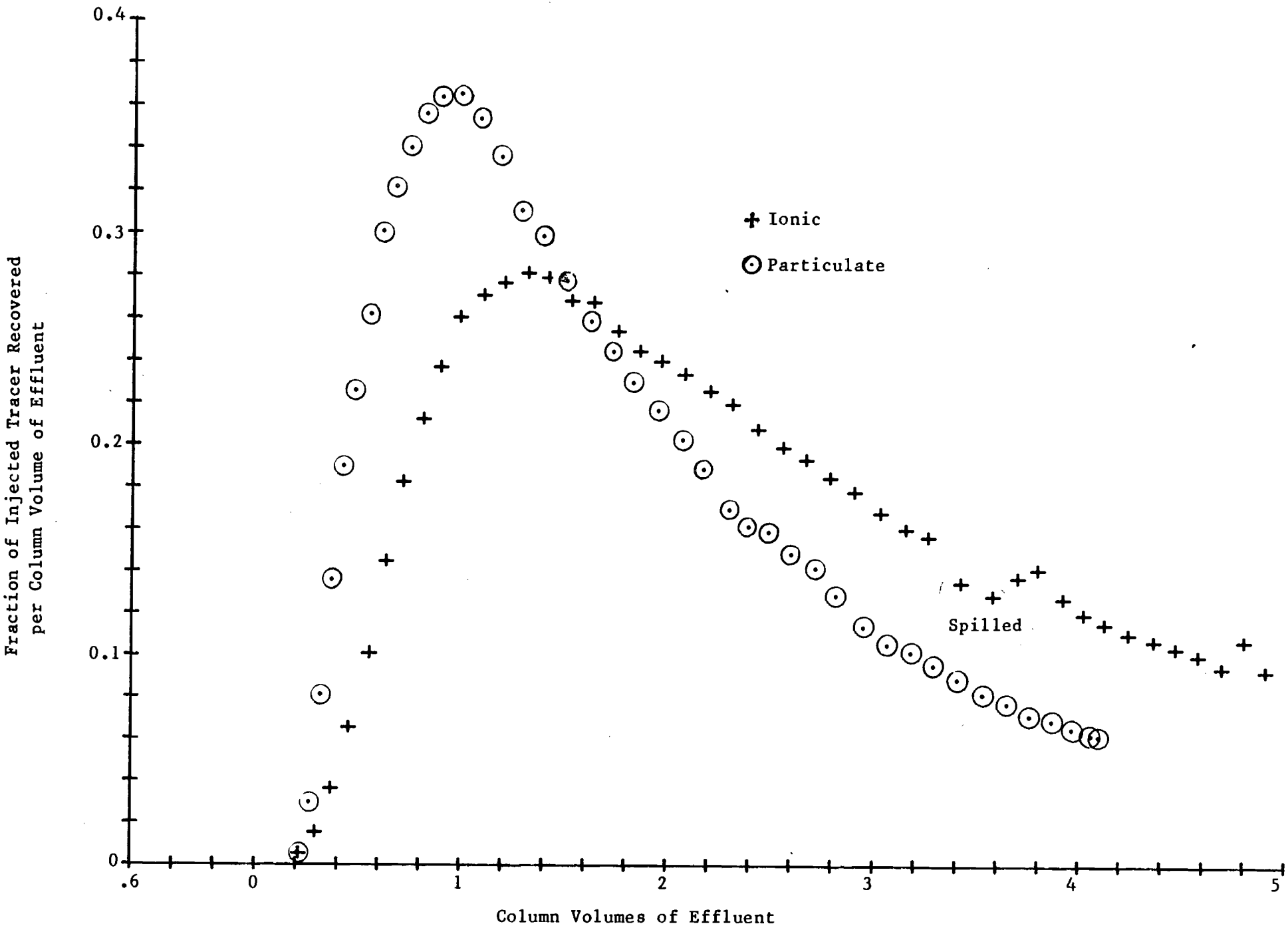

Fig. 5. Elution of Ionic and Particulate Tracers in the Small Column

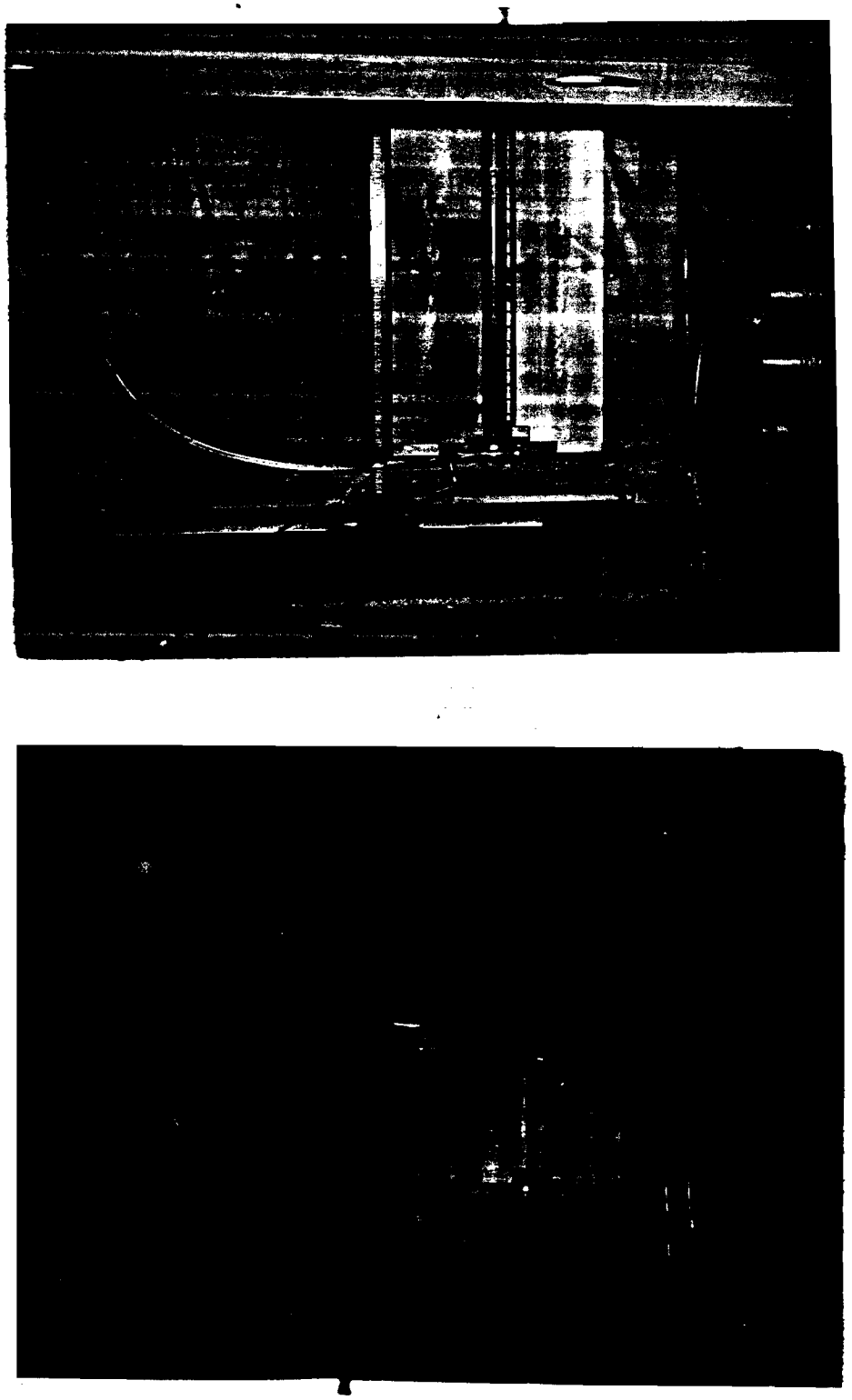

Fig. 6. Views of the Large Column and the Collimated Detector

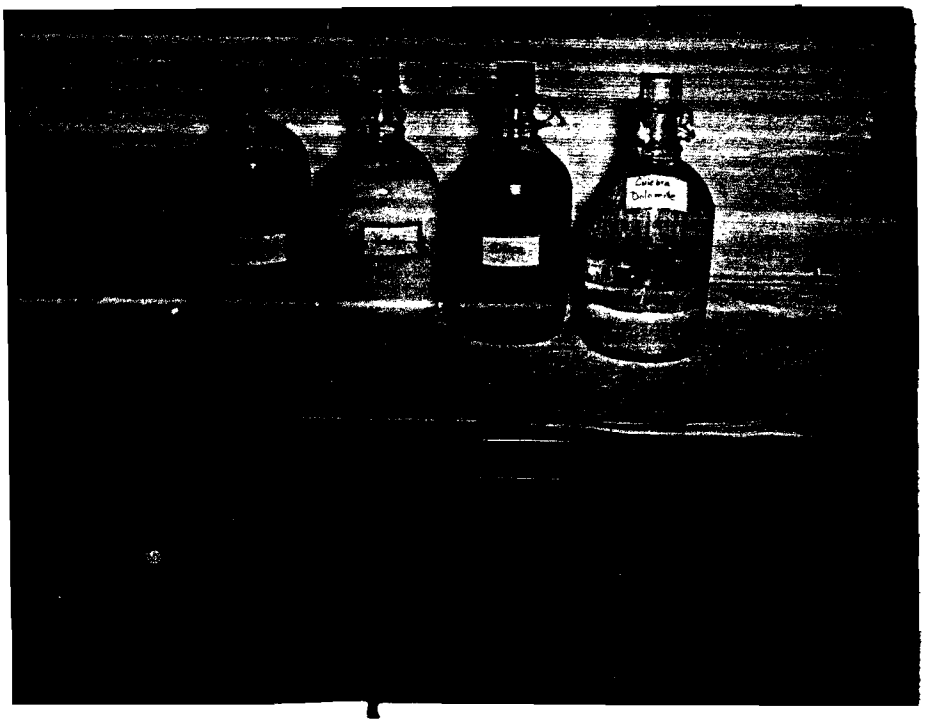

Fig. 7. View of Mineral Suspensions

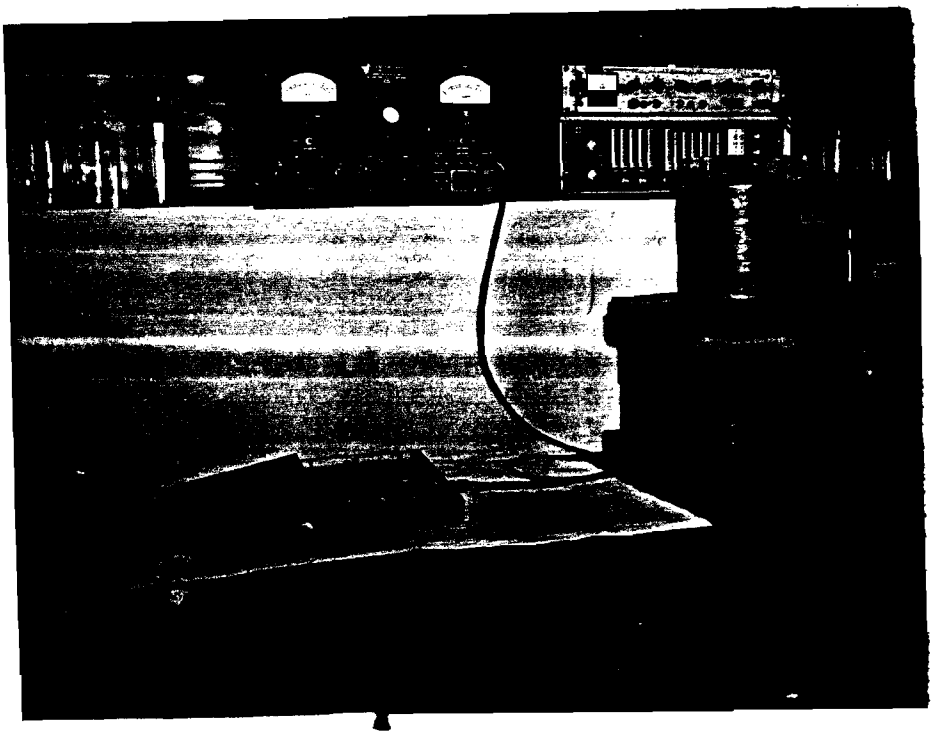

Fig. 8. High-voltage Electrophoresis Unit and Associated Power Supply

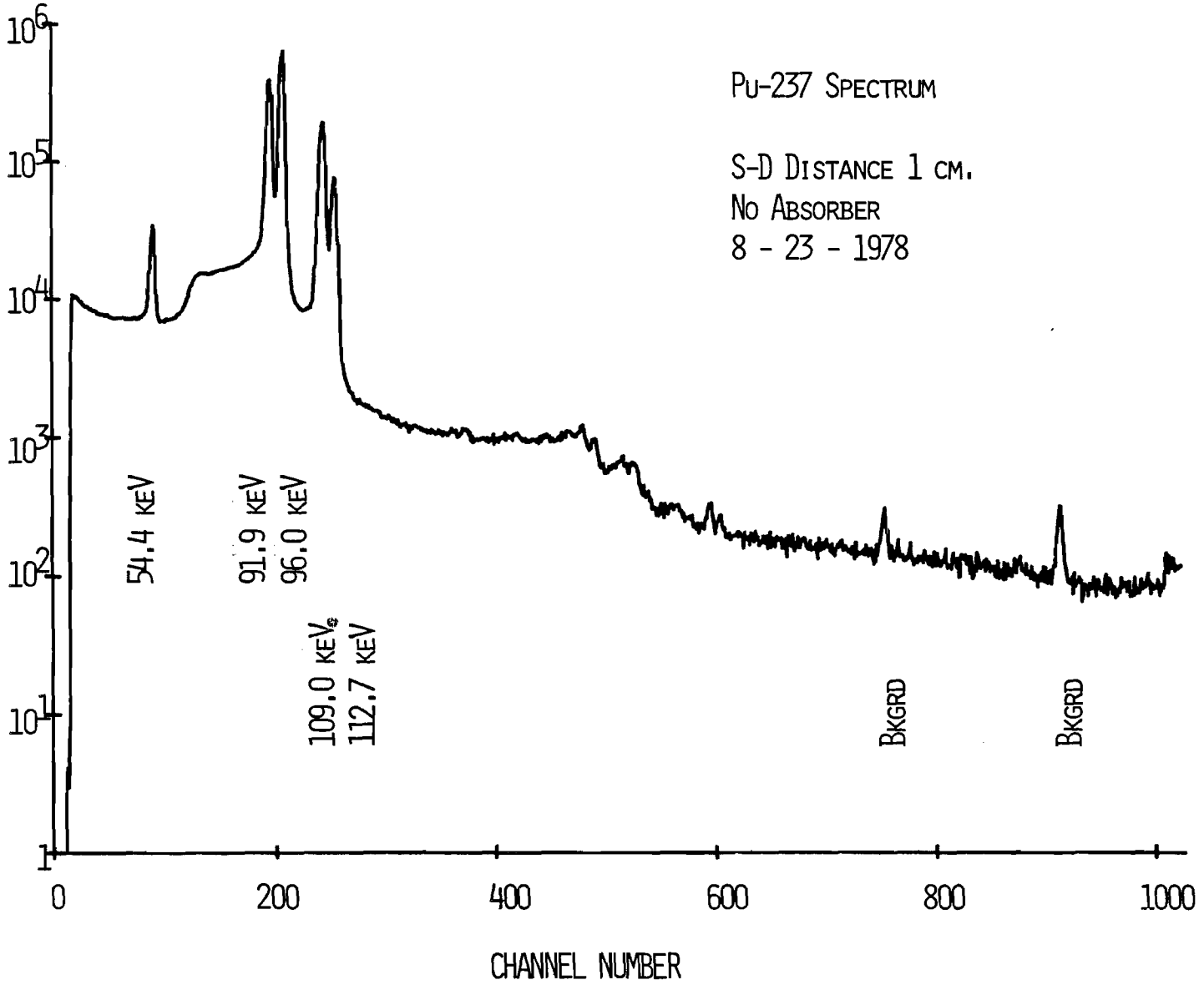

Fig. 9. Measured Pu-237 Spectrum

MOBILITY AND SORPTION PROCESSES OF RADIOACTIVE WASTE MATERIALS IN SUBSURFACE MIGRATION

Final Report
Spec. Agreement B-56084-A-H
Prime Contract EY-76-C-06-1830

by G. G. Eichholz and B. G. Wahlig

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Introduction

The safe disposal of high-level radioactive wastes is much in the public eye these days and in response to this interest, several major programs have been launched to identify suitable disposal sites, to qualify waste treatment processes as to effectiveness, permanence and cost, and to study possible migration paths and movement mechanisms by which a small portion of any buried solidified waste might conceivably be returned to the surface over a fairly long period of time. It is this latter problem area which is the subject of the DOE Prime Contract of which the present project constitutes a segment.

At the present time one envisages the disposal of solidified high-level radioactive wastes, preferably in processed and concentrated form, in deep crustal locations in artificial cavities in bedded salt or bed rock. Following a postulated incursion of water one may assume a slow leaching effect on the solid wastes, particularly if any crack development has occurred due to thermal or rock mechanical stresses, devitrification or anisotropic expansion effects. The slow movement of trace concentrations of waste products may then proceed in the form of tiny granules of solid waste or in soluble form. In the latter case dissolved ions would be expected to adsorb or plate out on exposed rock surfaces, shale or clay layers or on other fine particulates that may be present, suspended, in the aquifer. In the latter case, previous work at Georgia Tech has shown that radioactive pollutants may travel considerable distance, not necessarily at the velocity of the water, through a permeable bed layer. The present work has been directed to the study of two related phenomena:

1. the movement of submicron particles of a type expected near disposal

sites through aquifers of appropriate characteristics, and, 2. the sorption processes associated with the uptake of waste ions in trace concentrations on submicron particles and the measurement of subsequent partition coefficients leading to competitive transfer from the particles to surrounding media.

These two phenomena are interrelated since the competitive adsorption of dissolved ions on particulates or exposed rock surfaces will govern any partitioning occurring, as well as the dynamics of migration, and the movement of the postulated particulate carriers will be determined both by hydraulic factors and by interface effects.

The presence of fine particles of the type postulated here, at depth, has been questioned by some. However, almost every scenario envisaged in the situation the WISAP program addresses, assumes an incursion of water into a previously dry depository volume, in bed rock or bedded salt. This incursion usually requires some displacement or fracturing of rock and, hence, it is not unreasonable to expect the existence of both fine crystalline rock fragments and suspended clay particles in this water.[4,5] Anthigenetic clays and zeolites form in the early diagenesis of carbonate rocks, volcanic sediments and shales; since later diagenesis tends to be replacive, crystals of clays and other effective ion exchangers may be anticipated in deep groundwaters around rocks undergoing diagenetic alteration.[6-9] Thus strong circumstantial evidence suggests that fine particles do exist in deep groundwater and may migrate there.

Owing to extended delays in contract negotiations, the work under the project did not get formally under way until August 1, 1978. Related work, however, has been underway on a lesser scale for some time under

Georgia Tech auspices, so that the present report summarizes various measurements done in this context both before and since the initiation date. Because of the limited scale of the work, most data reported here must be considered to be preliminary in nature only.

Project Objectives

The purpose of the continuing project is the determination of all parameters that affect the long-range movement of trace concentration waste products from subsurface depositories by way of suspended particles. The particles are assumed to be naturally present in the aquifer from eroded rock material or colloidal aggregates, and to provide sorption sites for dissolved waste ions. The aqueous medium is de-aerated "pure" water, possibly modified by prolonged contact with fractured surrounding rock faces, or highly saline water in the case of bedded-salt repositories.

Factors that would be expected to affect mobility of the particulates are:

particle size and surface area
bed medium permeability
bed pore size
flow rate of water
temperature
particle material
bed material
particle shape
dielectric properties of particles.

Factors that would be expected to affect adsorption and desorption of trace material would include:

particle surface area
particle ion exchange capacity
trace element concentration
impurity concentration in water (hardness)
pH and E_h

valence of trace ions

K_D of bed medium

temperature

desorption parameters (concentration, displacement)

possible recoil effects

The work naturally falls into two major categories with various subtasks:

1. Mobility of particulates in permeable media

   pure water, saline water

   major trace elements (Pu, Tc, Zr, Cs)

   various particulates (clays, rock particles)

   various bed media (sand, rock, shale)

2. Sorption of trace elements on and off particulates

   various particulates and sizes

   pH, E_h of solution

   trace elements (as above)

   concentrations

   sorption rates

   surface area determinations

So far most of the work has concentrated on the first category, including the setting up of flow columns, the study of particulate movement, and the determination of detector sensitivity and resolution. However, work has been done on particle preparation and sizing, and some preliminary uptake studies. This work will be described in detail in the following sections.

Procedures and Methods

The tests on fine particle migration were made in columns containing beds of sand (for flow testing) or crushed rock (for sorption experiments)

through which particle-bearing solutions are allowed to flow. While the artificial fissure method of modeling field conditions has proved successful in studying dissolved radionuclides,[1] the affinity of fine particles for the surfaces under study is expected to be much smaller. Thus, columns of crushed rock are thought to be the most convenient way to provide sufficient numbers and path length to have a measurable effect upon particle behavior. The design and construction of the columns themselves will be discussed more fully below.

Water flows through the columns under the influence of gravity at pore velocities on the order of 10 km/yr. (In future experiments, metering pumps now on order will be used to drive the flow, which will allow better control of the flow at these or lower flow rates.) Traced particles in 1-2 m of water are injected by hypodermic syringe through a septum at the column inlet. The progress of the particles through the column is monitored in two ways--by external scanning detectors described below, and by counting successive portions of the column effluent.

The effluent counts are standardized to make it possible to calculate the fractional recovery of the injected tracer. For the two sizes of columns to be described below, the procedures for standardization differ as explained below. In both cases, the syringe is weighed before and after taking up the suspension of traced particles, after a portion is reserved for a standard, and after injection of the remainder of the tracer into the column. Knowing the masses of the standard and injected tracers and counting the standard in the same way as the effluent portions, one can relate the net count rates of the effluent to the total activity injected.

For the large column, the effluent portions are 20-50 mℓ, collected in disposable graduated beakers. The actual volume according to the graduations is recorded (for calculating concentrations) and the sample is brought to 50 mℓ total volume. All samples, including the calibration standard, are counted in 50 mℓ volumes. For the small column, it is more convenient to collect the samples in planchets, in fluid volumes of 1.2-3.5 mℓ. The samples are weighed immediately after collection and are then dried and reweighed to compute the sample volume. (The specific gravity of the samples is assumed to be a constant 1.0, although it must actually vary slightly from sample to sample. The total mass of the injected particles is only about 50 mg, however, and when distilled water is used to elute 50 or more samples, the error of assuming constant unit density is negligible.) All samples, including the calibration standard, are then counted as dried cakes in the planchets.

To date, only the natural sodium content of the particles has been used to trace them. This is convenient in testing equipment performance since activation to Na-24 in the Georgia Tech Research Reactor provides a readily available, inexpensive tracer of short half life. After about one week, unsatisfactory equipment can then be disassembled and modified without the need for decontamination. This tracer also suggests itself because high specific activity can be obtained, which is important in the detection of small portions of a 50 mg sample. Finally, the ready detectability of its gamma rays is an asset.

It is recognized, however, that this method will not be satisfactory for the main experimental activity, because the quality of interest is the behavior of radionuclides initially adsorbed on the surfaces of particles, and not the behavior of the particles themselves. In the bulk of the

experiments, then, Pu-237, Np-235, and perhaps Tc-95, obtained in the regular contractor distribution, will be the tracers of interest.

It may also prove desirable to follow both the particle and the adsorbed radionuclides in future experiments. While this may present certain logistical problems in obtaining the use of the requisite multichannel analyzers, it may also be the best alternative to the routine filtration of many small samples for which the initial volume of the sample as well as the activities of both the filter and the filtrate would have to be determined. The choice between these two possibilities has not yet been made.

Description of Apparatus

Columns

Two prototype columns have been constructed to date. Scale drawings of them are given in Fig. 1. Both are constructed of acrylic plastic tubing and sheet to minimize chemical interactions between the columns and the circulating solutions and to make visual inspection of the beds inside convenient. In constructing the prototypes it was necessary to use some brass fittings because of their ready availability, but polyethylene fittings are on order for use in the experimental columns. The only nonplastic materials expected to contact the solution in the experimental columns will be the rubber O-ring gaskets between the column flanges and their respective end caps, the fiberglass screen cemented over the entry hole in each end cap, and the iron-filled epoxy cement used throughout as cement and scalant. Each end cap is bolted to its respective flange in six places.

A large column, with 1 1/2" inside diameter (ID) and 27" bed length

was built first. According to published results on flow of fluids through beds of spheres packed in containers,[2] local velocity effects become negligible when the container to grain-diameter ratio (D/d) reaches 30-40. Thus there is a considerable margin of safety in using sand with a geometric mean size of 244 μm (0.0096 in., or $D/\bar{d} = 156$) for the bed in this column. The bed itself consists of 24 in. of this sand, restrained on each end by approximately 0.6 in. of 16-20 mesh crushed granite, 0.8 in. of 10-16 mesh granite, and the screen cemented to the end cap. Future work will use a less interactive end layer. Typical parameters for these beds are 37% porosity, 0.03 cm/sec permeability (both measured), and a calculated average effective pore size of approximately 50 μm.

It is realized that this granite complicates the assignment of effects observed, but two steps are planned to counteract this problem: 1) crushing some of the basalt chunks on hand to produce basalt gravel of the desired size; and 2) external scanning of the columns to determine where activity is bound.

Since it is desirable that the effluent from the column be representative of the flow through the whole cross-section of the bed, the end caps used initially incorporated mixing chambers of approximately 55 mℓ each. Some refluxing occurred in these chambers, however, as was readily visible with a $KMnO_4$ visible tracer. This effect is quantified in Fig. 2, which compares the elution profile of an injection of activated kaolin particles for the large column with the mixing end caps initially used and the non-mixing end caps shown in Fig. 1. ("Column volumes" are void volumes.) It is clear that although the total fraction of tracer carried through in the two cases is similar, the mixing end volumes smeared the elution profile over a larger volume even though the interactions between the particles and

the bed grains were unchanged. For this reason, the mixing end caps were eliminated.

The injected particles were not especially strongly affected by the bed, however, and behaved quite similarly in their elution profiles to an injection of an ionic tracer $^{24}Na_2CO_3$, as shown in Fig. 3. Although a smaller fraction of the kaolin than of the Na_2CO_3 was recovered, the particles were not significantly delayed compared to the ionic front.

Thus, it seemed desirable to use smaller grains in the bed to decrease the average pore size. Particles would then spend more of their time near grain surfaces, with correspondingly greater probability of attraction. The finer grains allowed the use of a smaller column also illustrated in Fig. 1. When this 0.5 in. ID column is loaded with 170-80 mesh (i.e., 88-178 μm diameter) grains, the minimum D/d ratio is 71, well within the range of acceptable local velocity effects. In this column, 17.5 in. of fine sand is restrained on either end by ~0.5 in. of coarse sand, 0.5 in. of 16-20 mesh granite, 0.5 in. of 10-16 mesh granite, and the fiberglass screen over the end cap opening. Typical parameters for such a bed are 40% porosity, 0.008 cm/sec hydraulic conductivity and average effective pore diameter of 23 μm.

The increased ability of the small column to restrain fine particles is shown in Fig. 4., which compares the elution profiles for kaolin in the large and small columns, normalized to eliminate the effect of their volume difference. Although similar total fractions of the tracer are recovered in the two cases, the small column clearly makes the retardation of fine particle migration a visible effect. However, the behavior of cations (as observed in a $^{24}Na_2CO_3$ test) is not much different from that of particulates, as was observed in the large column. This is shown as Fig. 5.

Besides having a greater effect on migrating species, the small column size also economizes on the use of bed material and radiotracer, and provides for less attenuation of radiation within the bed when an external scan is being taken. It is therefore anticipated that all future columns will be standardized versions of this smaller column, containing relatively fine grains of the medium of interest.

Detectors

Two kinds of scanning detectors have been tested. The first type is a Victoreen Thyrode thin-walled G-M tube in an end-on shield. This type was intended for use with the small column and is shown in several different views in Fig. 6. The shield provides 1.59 cm of lead around the whole length of the tube. Collimation is provided by a 1/2 in. x 1/2 in. square groove across the face of the shield. Fig. 6. also shows the rack provided for reproducible positioning of the shielded detectors when scanning the column. The overall effect is a rugged, inexpensive detector, whose chief problems are poor collimation and only moderate detection efficiency. Unfortunately, improving the collimation rapidly degrades the detection efficiency. Of course, the G-M detector is also incapable of energy discrimination.

Therefore, a change has been made to the Harshaw M12SHA3/3/4-X, a self-contained 0.472 in. x 0.500 in. thick NaI(Tℓ) collimated scintillation crystal assembly (originally designed for brain scanning). It was found experimentally that even with stricter collimation (3/8 in. wide x 1 in. deep compared to the 1/2 in. x 1/2 in.), the NaI detector was more sensitive than the G-M detector at photon energies up to 1.25 MeV, and is more sensitive by a factor of 5 for the low-energy photons from Pu-237. Although this system is considerably more expensive than the G-M system, its improved sensitivity, ease of collimation, and capability of energy discrimination make it preferable for the external scanning of the column. Therefore, the NaI detectors will be used for scanning in future work. Preliminary measurements have been done but improved collimator and positioning apparatus designs for the scanner are not yet completed.

The effluent detector is a 2 in. x 2in. NaI(Tℓ) detector housed in a stack of 2 1/1 in. radial width Pb shield rings. Its output is currently being counted simply in the discriminator mode, although pulse-height analysis may be employed in the future.

Fine Particles

One of the most important parts of this project is the preparation and characterization of suspensions of fine particles which will serve as carriers for radiotracers in the column experiments. To date, stable suspensions have resulted from the prolonged ball milling of kaolin, vermiculite, and silica. Samples of the suspensions obtained thusfar are shown in Fig. 7. In each case, the goal has been to create particles whose diameters are less than 1 μm.

Thusfar, the most success has been gained with kaolin. Approximately 100 mℓ of fine kaolin was ball milled in a one-quart ceramic jar about two-thirds filled with grinding balls and brim-full of distilled water. After 48 hrs. of milling, the fluid contents of the jar were poured off, the jar was rinsed out, and the resulting liquid was diluted to approximately 3 liters. This was allowed to settle for ~2 days and was then poured into a glass carboy. Approximately 25ℓ of suspension have been generated in this way and have remained opaque for about two months. The kaolin content of the suspension is ~ 30 mg/mℓ.

Raw (i.e., not heat-treated) vermiculite has been treated in a similar way, but has proven more resistant to grinding than kaolin. About 25ℓ of slightly cloudy suspension have been generated, but the vast majority of the solids generated are slightly too heavy to suspend stably--they settle out in times from two days to two weeks. Recycling these solids for

further milling has yielded some success.

In view of the difficulties encountered in grinding the two clays there is some doubt about the identity of the particles in the suspension resulting from grinding silica sand. Silica is much the hardest of the three minerals (Mohs' hardnesses are: kaolin, 2-2.5; vermiculite, ~1.5; quartz. ~7).[3] The suspicion is, then, that the particles in the suspension may be the results of abrasion of the grinding jar, and not silica at all. This possibility is further reinforced by the grinding of Culebra dolomite (hardness 3.5-4.0) under the same condition led to no stable suspension of particles. Thus, x-ray diffraction analysis of all the suspensions would appear to be in order to verify the identities of the particles; this has not yet been arranged for.

The particles may also be analyzed using a high-voltage electrophoresis unit constructed for this purpose and shown in Fig. 8. with its power supply. It remains to be seen whether the pore sizes of available chromatography papers are sufficiently large to permit particle migration and whether a satisfactory method for particle detection can be arrived at.

The next experiments to be undertaken will involve attempts to tag the particles with Pu-237. These await the arrival of water purification and testing equipment currently on order. It is vital to reproducibility that the water used in making the solutions start out pure and that conditions such as pH and total ionic strength be under control, since it may be expected that these will strongly affect the mechanisms and the reversibility of the sorption processes.

Pu-237 Spectrum

Since many of the standard references carry very sketchy descriptions of the photon spectrum, it was important to measure the energies and relative intensities with some accuracy to facilitate the choice of useful detection systems. The region of interest in this spectrum was calibrated using five peaks from Ga-133 (53.17 and 80.88 keV), Cd-109 (88.04 keV), and Co-57 (122.08 and 136.49 keV).

Conclusions

Because of the late date of finalization of the research contract and, hence, the limited manpower devoted to this project until recently, the results obtained so far are largely preliminary in nature. Work done has included some of the following:

setting up of two types of columns with detector systems;
determination of sensitivity and spatial resolution of the collimated GM and scintillation detectors
preparation of suspensions of kaolin particles
measurement of particulate movements through the bed with neutron-activated particles
determination of the Pu-237 γ-ray spectrum
planning of the next phases of the work, using several columns and a larger research group.

It is felt that reasonable progress has been made in getting ready for the major measurement program. Additional project personnel has been lined up and further equipment and supplies are being procured.

The results obtained so far illustrate the kind of differential movement between soluble tracers and active particulates that takes place in a permeable rock medium. It is hoped to obtain more definite results on the parameters concerned in the near future.

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Figure Captions

Fig. 1 Diagram of Prototype Columns

Fig. 2 Electron of Particulate Tracers in the Large Columns with "Mixing" and "Non-mixing" End Caps

Fig. 3 Electron of Ionic and Particulate Tracers in the Large Column

Fig. 4 Electron of Particulate Tracers in the Large and Small Columns

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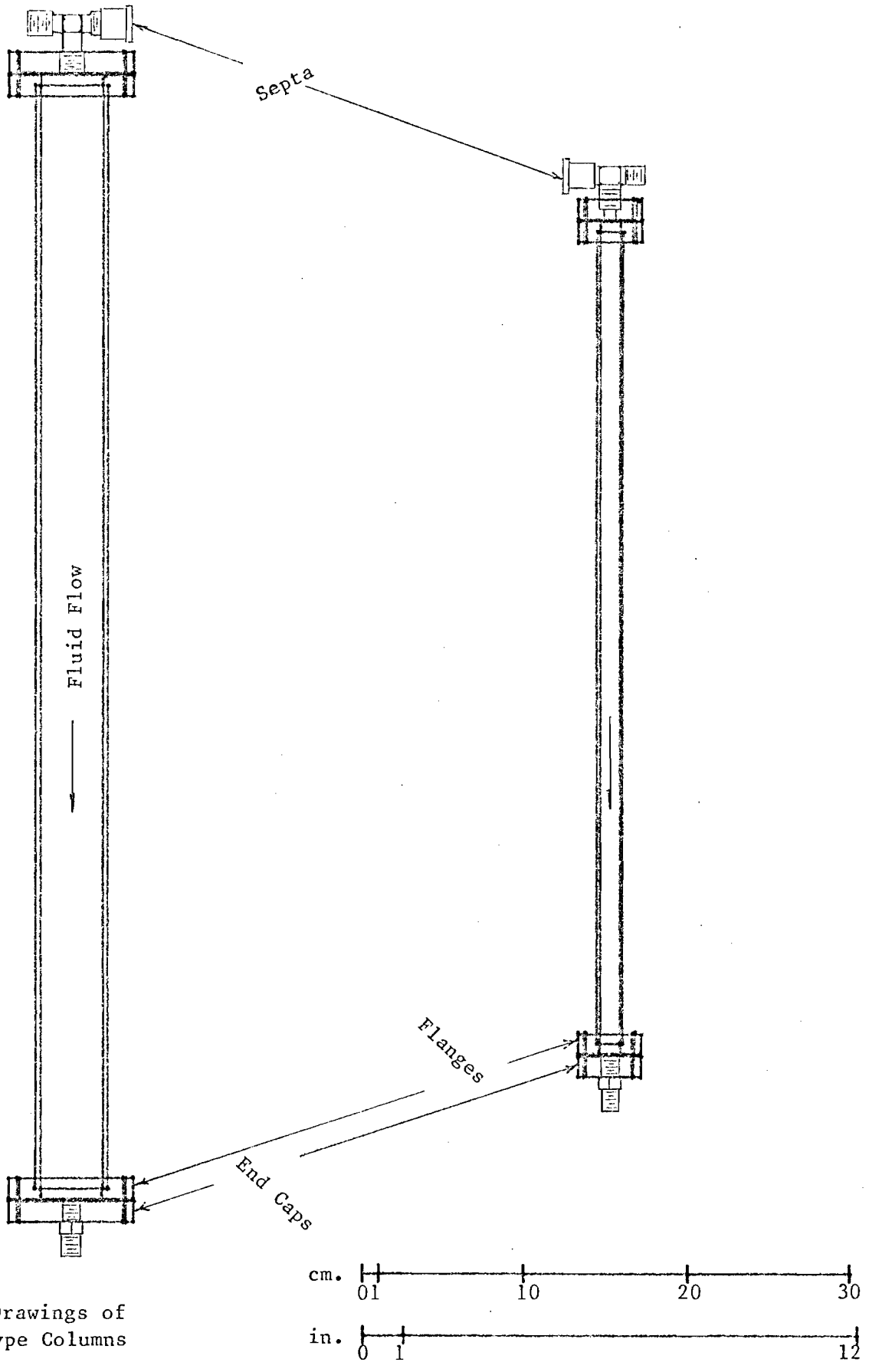


Fig. 1. Scale Drawings of Prototype Columns

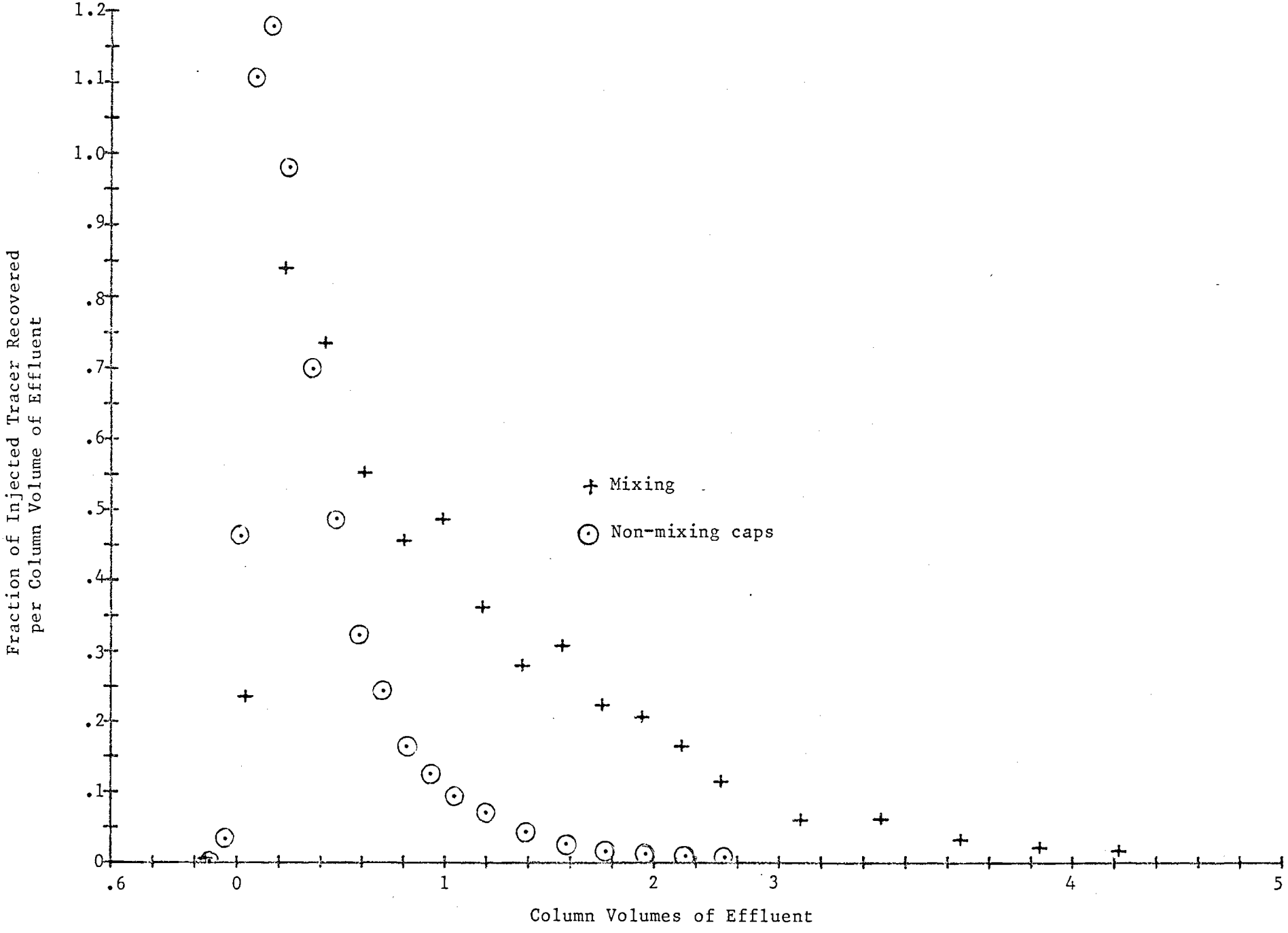
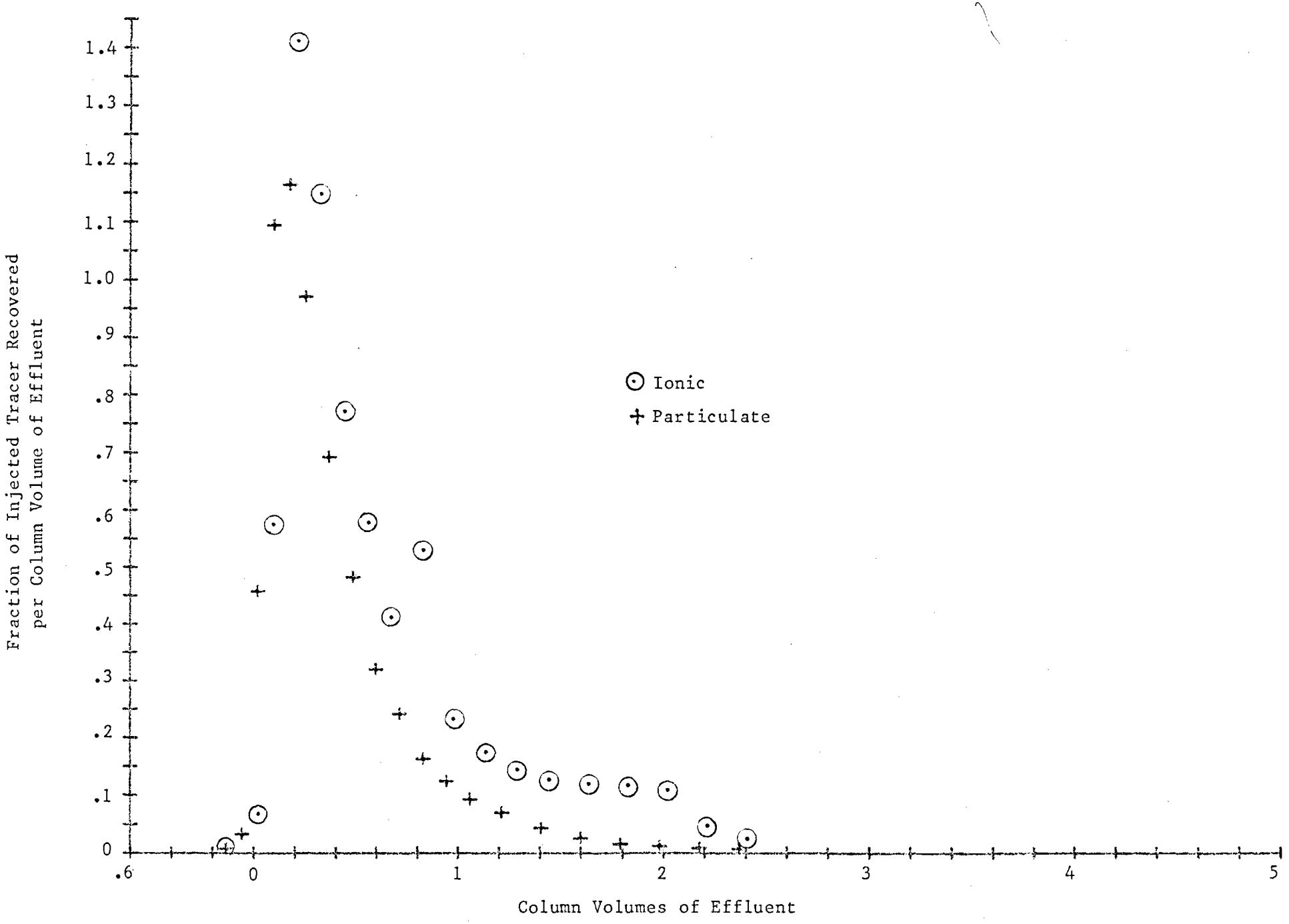


Fig. 2. Elution of Particulate Tracers in the Large Column with Mixing and Non-Mixing End Cap



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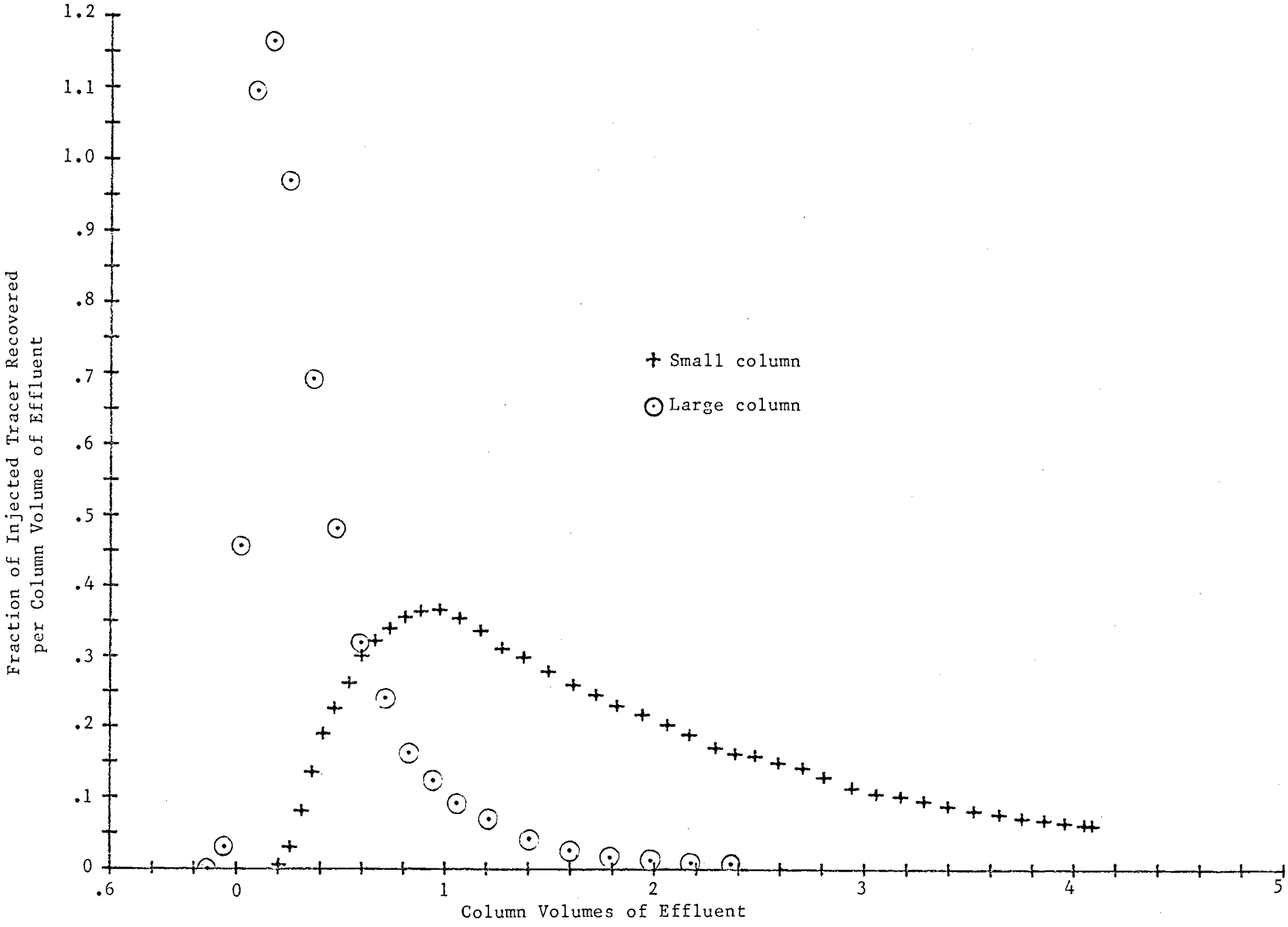

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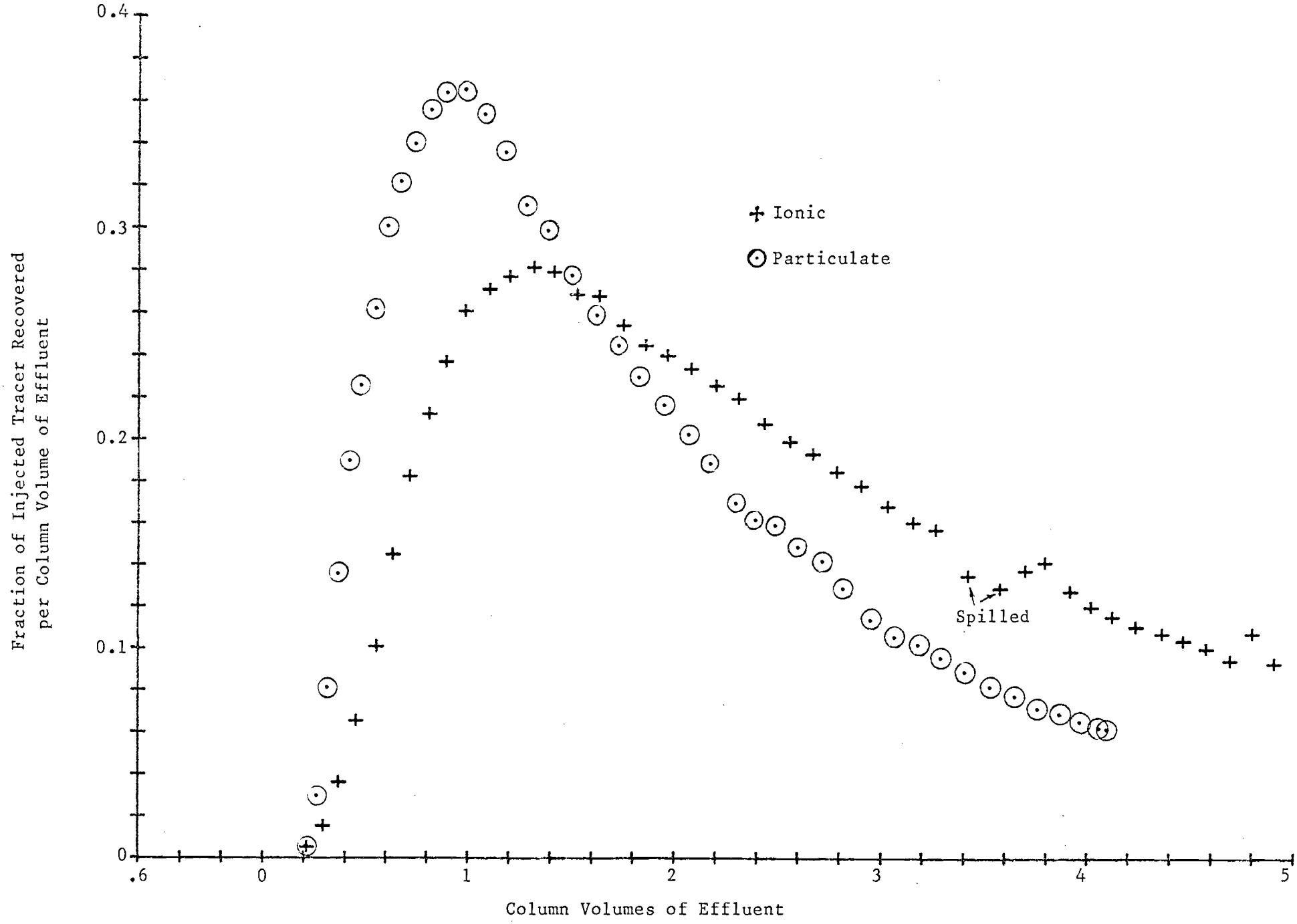

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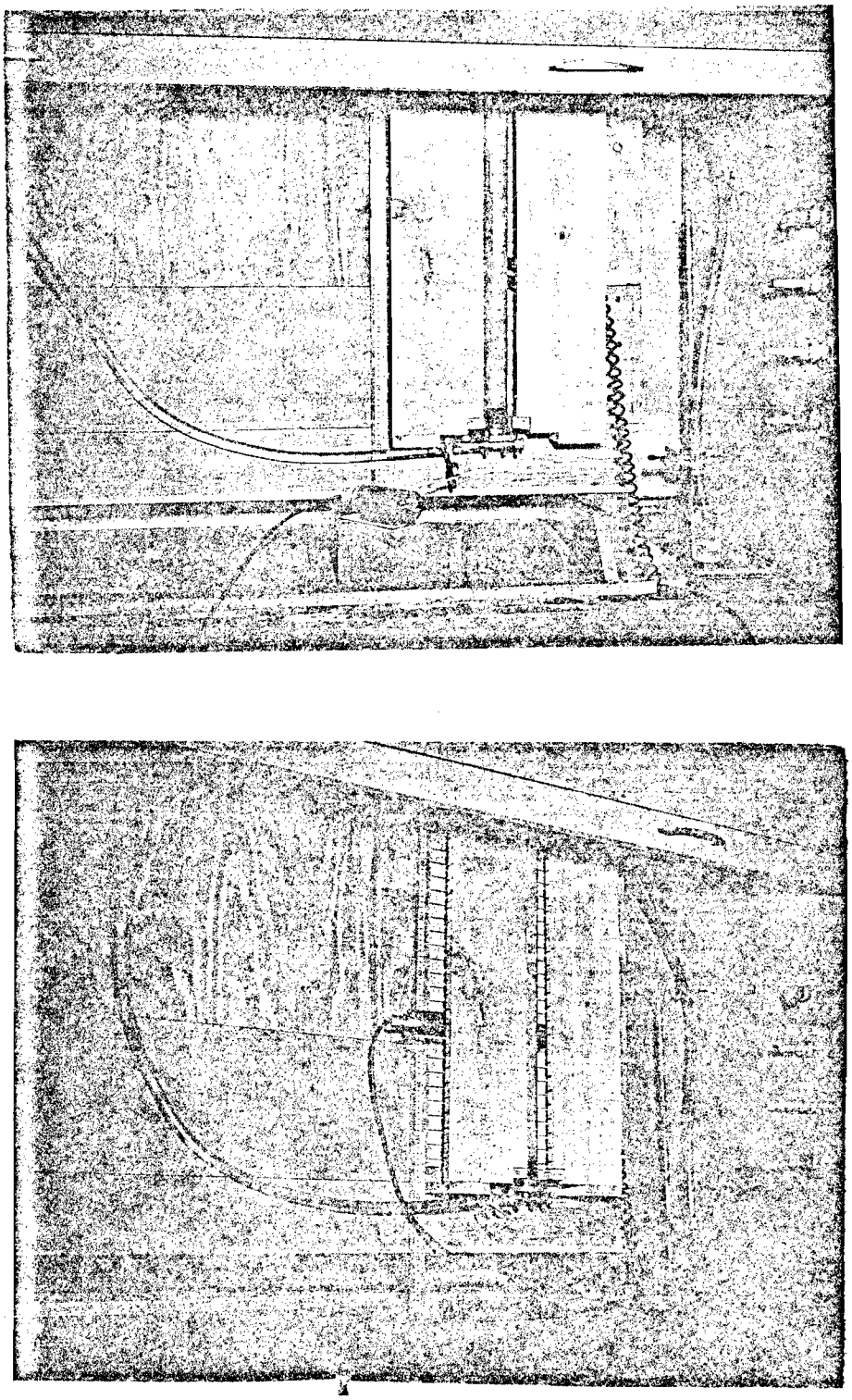

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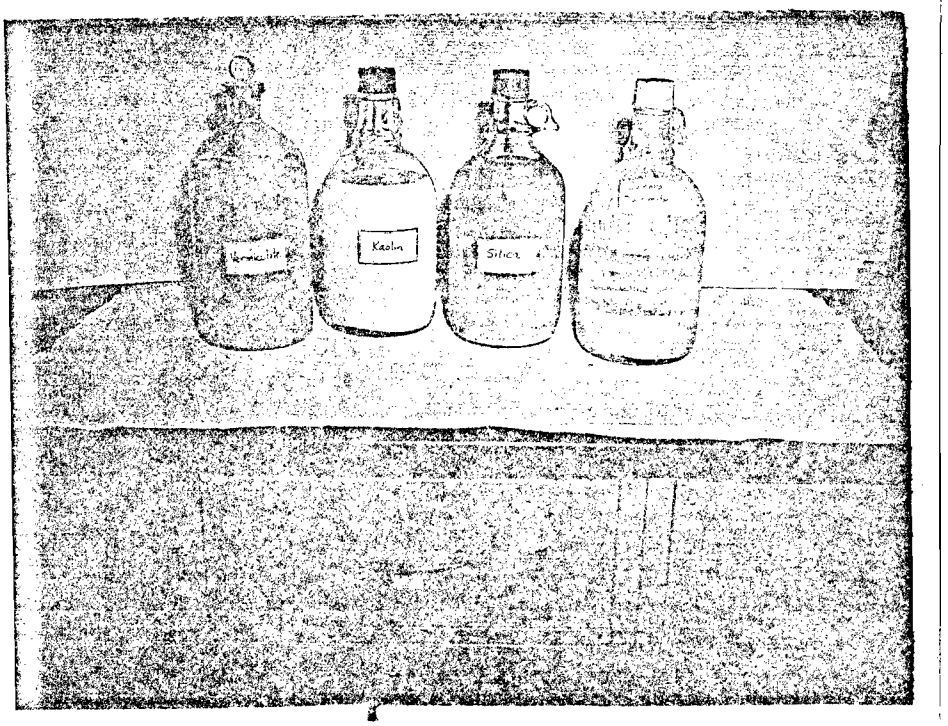

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